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CHEMISTRY OF 3,4-DIMETHYLPHOSPHOLYL ANION IN THE COORDINATION SPHERE OF TUNGSTEN: SYNTHESIS AND X-RAY CRYSTAL STRUCTURE ANALYSIS OF (η^5-3,4-DIMETHYLPHOSPHOLYL)TRICARBONYL-IODOTUNGSTEN

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Abstract—The reaction of the 3,4-dimethylphospholyl anion with $W(CO)_6$ and $W(CO)_5THF$ yields, according to the experimental conditions and stoichiometries, the η^1-P complex $(Me_2C_4H_2\bar{P})W(CO)_5$ or the μ^2-P complex $(Me_2C_4H_2\bar{P})[W(CO)_5]_2$. We have compared the reactivities of the free phospholyl anion and its P–$W(CO)_5$ and P–$[W(CO)_5]_2$ complexes toward H^+, $ClSnR_3$, S_8 and iodine. The most spectacular result has been observed when allowing iodine to react with the P–$[W(CO)_5]_2$ complex. The new η^5-$(Me_2C_4H_2P)W(CO)_3I$ complex has been obtained and characterized by X-ray crystal structure analysis. A typical nucleophile such as hydroxide ion attacks this η^5-complex not at the W—I bond as expected, but at the P atom with breaking of the P—W bond and formation of a η^4-diene complex. The lone pair at P remains able to coordinate with another metallic centre.

In a series of preceding papers, we have shown that complexation of the phosphorus lone pair by a pentacarbonyltungsten unit drastically alters the chemistry of tervalent phosphorus compounds. For example, strained phosphorus heterocycles gain additional stability[1–3] and decomposition of RP(H)X species through reductive elimination at phosphorus is quenched in many cases.[4–6] From another standpoint, if η^5-phospholyl complexes have been described with transition metals of the titanium (Zr[7]), manganese (Mn[8,9] or Re[9]), iron[10,11] and cobalt[12] families, no such complex has been reported till now with a metal of the chromium subgroup. These two kinds of considerations prompted us to study the chemistry of the well-known phospholyl anions[13] in the coordination sphere of tungsten.

EXPERIMENTAL

NMR spectra (chemical shifts in ppm from internal Me_4Si for ^1H and ^{13}C, and from external H_3PO_4 for ^{31}P; δ positive for downfield shifts in all cases) were recorded on a Bruker WP 80 instrument respectively at 80.13, 20.15, and 32.44 MHz. Mass spectra [electronic impact desorption (EID) or chemical ionization desorption (CID)] were recorded on a Nermag R10-10 spectrometer by Mr Charré (SNPE). All reactions were carried out under argon. Chromatographic separations were performed on deoxygenated silical gel columns (70–230-mesh, Riedel de Haën).

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Preparation of phospholyllithium–tungsten complexes

[η^1 - P - 3,4 - *dimethylphospholyllithium*]*pentacarbonyltungsten* (**3**). Solid tungsten hexacarbonyl (3.5 g, 10 mmol) was added to 10 mmol of 3,4-dimethylphospholyllithium (**2**) (see Ref. 14) in THF (80 cm^3). After stirring at room temperature for 8 h, the ^{31}P NMR spectrum of the reaction mixture showed a single signal at -54.8 ppm corresponding to the monotungsten complex. To a sample of the solution in a NMR tube was added an excess of methyl iodide. After 10 min at room temperature, the ^{31}P NMR spectrum showed a single signal corresponding to the known [1,3,4-trimethylphosphole]pentacarbonyltungsten complex (**4**) at -8.4 ppm [$^1J(^{31}\mathrm{P}-^{183}\mathrm{W})$ 207.5 Hz].

[μ^2 - P - 3,4 - *dimethylphospholyllithium*]*decacarbonylditungsten* (**5**). To the preceding solution of phospholyllithium complex **3** (10 mmol) was added one equivalent of tungsten hexacarbonyl (3.5 g). After 5 h of reflux, the ^{31}P NMR spectrum showed a single signal at -99.5 ppm [$^1J(^{31}\mathrm{P}-^{183}\mathrm{W})$ 141.5 Hz, intensities 1:6:1]. The same result was obtained by refluxing one equivalent of phospholyllithium (**2**) for 8 h with two equivalents of $W(CO)_6$, or by reaction of anion **2** with $W(CO)_5$THF.[5]

Preparation of [η^1-P-3,4-*dimethylphosphole*]*pentacarbonyltungsten* (**6**)

Methane sulfonic acid (1.9 g, 20 mmol) in 20 cm^3 of CH_2Cl_2 was treated at room temperature by a solution of 10 mmol of the phospholyllithium complex **3**. After vacuum distillation of the THF, the residue was chromatographed with toluene leading to a mixture which was dissolved in 1 cm^3 of CH_2Cl_2 and 50 cm^3 of hexane. Filtration over diatomaceous silica and distillation of the solvents gave a partially crystallized oil. Yield 2.5 g (ca 47%). The ^{31}P NMR spectrum in CH_2Cl_2 showed a major signal at -46.1 ppm [$^1J(^{31}\mathrm{P}-^{183}\mathrm{W})$ 232 Hz, ^1J(P–H) 322 Hz] and a minor signal at 20.2 ppm [$^1J(^{31}\mathrm{P}-^{183}\mathrm{W})$ 224.5 Hz]. A recrystallized sample at EtOH (pale yellow solid) gave the same spectrum.

[η^1 - P,η^1 - P′ - 3,3′,4,4′ - *tetramethyl* - 2,5 - *dihydro* - 1,1′ - *biphospholyl*]*decacarbonylditungsten* (**7**)

To a solution of **3** (10 mmol in THF), cooled at about -40°C, was added 3.4 g (20 mmol) of 4-toluene sulfonic acid monohydrate. The solvent was vacuum distilled and the residue chromatographed with CH_2Cl_2 leading to 7.4 g of a solid; m.p. 190°C (yield 85%). An analytical sample was recrystallized in acetone; pale yellow crystals; m.p. 195°C; ^{1}H NMR ($CDCl_3$) phosphole ring: δ 2.20 [pseudo t, ^4J(H–P) ~ 1 Hz, 6H, CH_3], 6.20 [d, ^2J(H–P) 37.4 Hz, 2H, $=$CH]; phospholene ring: δ 1.7 (s, 6H, CH_3), 2.53 and 2.96 [AB system, $^2J(H_A-H_B)$ 17.6 Hz, 4H, CH_2]; ^{13}C–{^{1}H} NMR [$CDCl_3$) phosphole ring: δ 17.7 [d, ^3J(C–P) 11 Hz, CH_3], 128.8 [pseudo q, ^1J(C–P) 30.5 Hz, ^2J(C–P) 2.5 Hz, $=$CH], 154.0 [pseudo q, ^2J(C–P) 6.1 Hz, ^3J(C–P) 3.7 Hz, $=\mathrm{C}\!<$]; phospholene ring: δ 16.2 [d, ^3J(C–P) 6 Hz, CH_3], 43.3 [pseudo q, ^2J(C–P) 18.3 Hz, ^3J(C–P) 4.9 Hz, CH_2], 131.9 (s, $=\mathrm{C}\!<$) and δ 196.1 (d, CO), 197.0 (d, CO); IR ($CHCl_3$) ν(CO) 2080, 2070, 1950, 1930 cm^{-1}; mass spectrum (EID, 70 eV, ^{184}W) m/z (relative intensity): 872 [M (50%)], 437 [M$-$phosphole ring (50%)], 435 [M$-$phospholene ring (40%)]. Found: C, 30.4; H, 2.1; P, 7.0; W, 42.1%. Calc. for $C_{22}H_{18}O_{10}P_2W_2$: C, 30.3; H, 2.1; P, 7.1; W, 42.2%.

[η^1 - P - 3,4 - *dimethyl* - 1 - *triphenylstannyl phosphole*]*pentacarbonyltungsten* (**9**)

To the phospholyllithium complex (**3**) (10 mmol in 80 cm^3 of THF) was added at room temperature triphenyltin chloride (4.25 g, 11 mmol) in 20 cm^3 of THF. After 30 min of stirring, the solvent was vacuum distilled and the residue chromatographed in toluene on silica gel dried at ca 150°C under 10^{-2} mmHg. Evaporation of the solvent led to 5.4 g (yield 68.5%) of an orange oil. ^{1}H NMR ($CDCl_3$): δ 1.82 (poorly resolved d, 6H, CH_3), 6.60 [d, ^2J(H–P) 41.2 Hz, 2H, CH], 7.4 (m, 15H, Ph); ^{13}C–{^{1}H} NMR: δ 17.8 [d, ^3J(C–P) 9.7 Hz, CH_3], 129.7 [d, ^1J(C–P) 40.3 Hz, $=$CH], 128.5–132.2 (m, aromatic CH), 135.8–138.9 (m, arom. $=\mathrm{C}\!<$), 152.9 [d, ^2J(C–P) 4.9 Hz, $=\mathrm{C}\!<$], 196.5 [d, ^2J(C–P) 6.1 Hz, CO], 200.1 [d, ^2J(C–P) 20.7 Hz, CO], ^{119}Sn–{^{1}H} NMR (C_6D_6): δ Me_4Sn (neat) -88.4 [d, $^1J(^{119}\mathrm{Sn}-^{31}\mathrm{P})$ 92.8 Hz]; IR (hexane): ν(CO) 2068, 1985, 1950 cm^{-1}.

[η^1 - P - 3,4 - *dimethyl* - 1 - *methylthiophosphole*]*pentacarbonyltungsten* (**10**)

Solid sulphur (0.35 g, 11 mmol) was added to the THF solution of complexed phospholyllithium (10 mmol) at room temperature. After 30 min of stirring the thioanion formation was checked by ^{31}P NMR (resonance at 14.9 ppm in THF). Methyl iodide (1.56 g, 11 mmol) was then added. The reaction mixture was stirred 30 min more and the THF was distilled under vacuum. Chromatography of the residue with toluene followed by solvent distillation led to 3.25 g (yield ca 70%) of complex **10**; m.p. 105°C (orange yellow crystals). ^{1}H NMR (CDCl$_3$): δ 1.77 [d, ^{3}J(H–P) 9.0 Hz, 3H, SCH$_3$], 2.2 [d, ^{4}J(H–P) 1.0 Hz, 6H, CH$_3$], 6.13 [dd, ^{2}J(H–P) 38.8 Hz, ^{4}J(H–H) 1.0 Hz, 2H, =CH]; ^{13}C–{^{1}H} NMR (CDCl$_3$): δ 13.65 [d, ^{2}J(C–P) 2.4 Hz, SMe], 16.75 [d, ^{3}J(C–P) 12.2 Hz, C–$\underline{\mathrm{M}}$e], 127.6 [d, ^{1}J(C–P) 37.6 Hz, =CH], 151.45 [d, ^{2}J(C–P) 9.7 Hz, $=C\langle$], 195.4 [d, ^{2}J(C–P) 7.3 Hz, CO]; IR (hexane): ν(CO) 2073, 1947 cm^{-1}. Found: C, 30.0; H, 2.0; P, 6.3; S, 6.4%. Calc. for $C_{12}H_{11}O_5PSW$: C, 29.9; H, 2.3; P, 6.4; S, 6.6%.

3,4-*Dimethyl*-1-*methylthiophosphole* P-*sulphide* (**13**)

To a solution of 10 mmol of **2** in THF, was added 2.2 equivalents of solid sulphur. After 10 min, the formation of the intermediate thioanion **13a** was controlled by ^{31}P NMR [δ(^{31}P) 63.9, t, ^{2}J(P–H) 29.3 Hz] and then 1.7 g (ca 12 mmol) of methyl iodide in 5 cm^3 of THF was added. The reaction mixture was vacuum concentrated and the residue chromatographed with hexane–CH$_2$Cl$_2$ (80 : 20) leading to 1.3 g (yield 65.5%) of **13**; m.p. 85°C (pale yellow crystals); ^{1}H NMR (CDCl$_3$): δ 2.1 [q, ^{4}J(H–P) 2 Hz, ^{4}J(H–H) 1 Hz, 6H, C—CH$_3$], 2.3 [d, ^{3}J(H–P) 14.5 Hz, 3H, SCH$_3$], 6.0 [dd, ^{2}J(H–P) 33.0 Hz, 2H, =CH]; ^{13}C–{^{1}H} NMR (CDCl$_3$): δ 12.7 [d, ^{3}J(C–P) 2.9 Hz, C–CH$_3$], 16.8 [d, ^{2}J(C–P) 19.5 Hz, S—CH$_3$], 123.2 [d, ^{1}J(C–P) 82.0 Hz, =CH], 151.7 [d, ^{2}J(C–P) 20.5 Hz, $=C\langle$]; mass spectrum (EID) m/z (relative intensity): 190 [M (26%)], 143 [M − SMe (100%)]. Found: C, 44.3; H, 5.8; P, 16.3%. Calc. for $C_7H_{11}PS_2$: C, 44.2; H, 5.8; P, 16.3%.

[η^1 - P,η^1 - P′ - 3,3′,4,4′ - *tetramethyl* - 1,1′-*biphospholyl*]*decarbonylditungsten* (**14**)

A solution of iodine (1.27 g, 5 mmol) in 10 cm^3 of THF was slowly added at room temperature to **3** (10 mmol in THF). The reaction mixture was vacuum contentrated and the residue chromatographed with first CH$_2$Cl$_2$ and then ethyl acetate. Distillation of the solvents led to 2.4 g (yield 55%) of yellow orange crystals; m.p. (dec.) 230°C. An analytical sample was recrystallized in THF; m.p. (dec.) 233–236°C; ^{1}H NMR (THF-d_8): δ 2.24 (pseudo t, 12H, CH$_3$), 6.63 [m, ^{2}J(H–P) 39.5 Hz, 4H, CH]; ^{13}C–{^{1}H} NMR (THF-d_8): δ 17.45 (pseudo t, CH$_3$), 130.9 (pseudo t, =CH), 156.2 (pseudo t, $=C\langle$), 195.5 (d, CO); IR (CHCl$_3$), ν(CO) 2065, 1980, 1950 cm^{-1}; mass spectrum (EID, ^{184}W) m/z (relative intensity): 870 [M (50%)], 590 [M − 10CO (20%)], 435 [M/2 (100%)]. Found: C, 30.4; H, 1.8; W, 42.5%. Calc. for $C_{22}H_{16}O_{10}P_2W_2$: C, 30.4; H, 1.8; W, 42.3%.

Complex **14** was also obtained by reaction of 3,3′,4,4′-tetramethyl-1,1′-biphospholyl[4] with two equivalents of W(CO)$_5$THF in THF.

[η^5 - 3,4 - *Dimethylphospholyl*]*tricarbonyliodotungsten* (**15**) *and* [η^1 - P - (η^5 - 3,4 - *dimethylphospholyl*) *tricarbonyliodotungsten*]*pentacarbonyltungsten* (**17**)

To a solution of 10 mmol of the ditungsten complex **5** was added iodine (11 mmol in 10 cm^3 of THF) at room temperature. After 2 h of stirring, the reaction mixture gave a single or major ^{31}P NMR signal at −31.5 ppm. The solvent was vacuum distilled and the residue dissolved in a small amount of CH$_2$Cl$_2$. In this solution, the ^{31}P NMR resonance at −31.5 decreased to the benefit of a new signal at −11.2 ppm. A large amount of hexane was then added and the mixture was filtered through a column of diatomaceous silica. The solvent was removed and the residue chromatographed on acidic silica gel giving first, by elution with hexane + 20% of CH$_2$Cl$_2$, complex **15**, then, with CH$_2$Cl$_2$, complex **17**.

Complex **15**: 1.9–2.7 g (yield 37.5–53.5%), dark purple crystals; m.p. 112°C; ^{1}H NMR (CDCl$_3$): δ 2.48 (s, 6H, CH$_3$), 5.16 [d, ^{2}J(H–P) 35.2 Hz, 2H, =CH]; ^{13}C–{^{1}H} NMR (CDCl$_3$): δ 16.6 (s, CH$_3$), 100.1 [d, ^{1}J(C–P) 67.1 Hz, =CH], 126.8 [d, ^{2}J(C–P) 8.5 Hz, $=C\langle$], 207.7 and 221.5 (CO); IR (hexane) ν(CO) 2037, 1968, 1957, 1945 cm^{-1}; mass spectrum (EID, ^{184}W) m/z (relative intensity): 506 [M (15%)], 478 [M − CO (50%)], 450 [M − 2CO (30%)], 422 [M − 3CO (75%). Found: C, 21.6; H, 1.5; I, 25.0; P, 6.1%. Calc. for $C_9H_8IO_3PW$: C, 21.4; H, 1.6; I, 25.1; P, 6.1%.

Complex **17**: in addition to the chromatographed product, another fraction of complex **17** was recovered by washing the celite column with CH$_2$Cl$_2$. Recrystallization of the two fractions gave 1–3 g (yield 12–36%) of orange crystals; m.p. (dec.) 185–187°C; ^{1}H NMR (CDCl$_3$): δ 2.60 (s, 6H, Me), 5.10 [d, ^{2}J(H–P) 32.0 Hz, 2H, =CH]; ^{13}C–{^{1}H} NMR (CD$_3$COCD$_3$): δ 15.75 [d, ^{3}J(C–P) 3.6 Hz, CH$_3$], 94.4 [d, ^{1}J(C–P) 7.3 Hz, =CH], 124.8 (s, $=C\langle$), 193.4 [d, ^{2}J(C–P) 7.3 Hz, W(CO)$_5$]; IR (CHCl$_3$): ν(CO) 2085, 2040, 2000 (sh), 1975, 1957 cm^{-1}; mass spectrum (CID, iso-C$_4$H$_{10}$, ^{184}W) m/z (relative intensity): 830 [M (90%)], 703 [M − I (40%)], 506

[M – W(CO)$_5$ (100%)]. Found: C, 20.4; H, 0.9; I, 15.2; P, 3.7; W, 44.4%. Calc. for $C_{14}H_8IO_8PW_2$: C, 20.3; H, 1.0; I, 15.3; P, 3.7; W. 44.3%.

The ditungsten complex **17** was also obtained by allowing the η^5-phospholyltungsten complex **15** to react with W(CO)$_5$THF in THF.

Tetramethylammonium [η^4-C$_4$-3,4-*dimethyl*-1-*oxophosphole*]*tricarbonyliodotungstate* (**16**)

To the η^5-phospholyl complex **15** (1.02 g, 2 mmol) in 30 cm^3 of CH$_2$Cl$_2$ was added 1.03 cm^3 (2 mmol) of a 20% methanolic solution of tetramethylammonium hydroxide. The reaction mixture turned from dark red to orange. Filtration on diatomaceous silica followed by vacuum concentration of the filtrate led to an orange oil which crystallized. The solid was sucked dry on sintered glass after washing with a mixture of hexane and CH$_2$Cl$_2$ (50:50). Yield 0.9 g (75%) orange crystals; m.p. 188°C; ^{1}H NMR (CD$_3$COCD$_3$): δ 2.26 (s, 6H, CH$_3$), 3.01 [dd, ^2J(H–P) 14.1 Hz, ^3J(H–H) 0.95 Hz, 2H, =CH], 3.43 [t, ^1J(^{1}H–^{14}N) 0.6 Hz, 12H, NCH$_3$], 7.36 [dt, ^1J(H–P) 530.2 Hz, 1H, PH]; ^{13}C–{^{1}H} NMR (CD$_3$COCD$_3$): δ 16.7 [d, ^3J(C–P) 3.6 Hz, CH$_3$], 52.4 [d, ^1J(C–P) 78.1 Hz, =CH], 56.0 [t, ^1J(^{13}C–^{14}N) 3.6 Hz, NCH$_3$], 90.1 [d, ^2J(C–P) 14.6, $=C\langle$], 218.2 and 228.6 (CO); IR (KBr): ν(PH) 2380 cm^{-1}; ν(PO) 1177 cm^{-1}; ν(CO) 1990, 1915, 1880 cm^{-1}. Found: C, 26.7; H, 3.9; N, 2.3; P, 5.0%. Calc. for $C_{13}H_{21}INO_4PW$: C, 26.1; H, 3.5; N, 2.3; P, 5.2%.

X-ray data collection and processing

Suitable single crystals of **15** were obtained by slow evaporation of CH$_2$Cl$_2$–hexane solutions at room temperature under argon. A systematic search in reciprocal space using a Philips PW 1100/16 automatic diffractometer showed that crystals of **15** belong to the monoclinic system. The unit-cell dimensions and their standard deviations were obtained and refined at –100°C with Mo-K_α radiation (λ = 0.71073 Å) by using 25 carefully selected reflections and the standard Philips software. Crystal data: $C_9H_8O_3PIW$, $M = 506$, $a = 7.325(3)$ Å, $b = 14.545(6)$ Å, $c = 12.169(5)$ Å, $\beta = 103.46(2)$, $V = 1261$ Å^3, $Z = 4$, $d_c = 2.665$ g cm^{-3}, $d_o = 2.63 \pm 0.02$ g cm^{-3}, $\mu = 118.93$ cm^{-1}, $F(000) = 912$, space group $P2_1/n$.

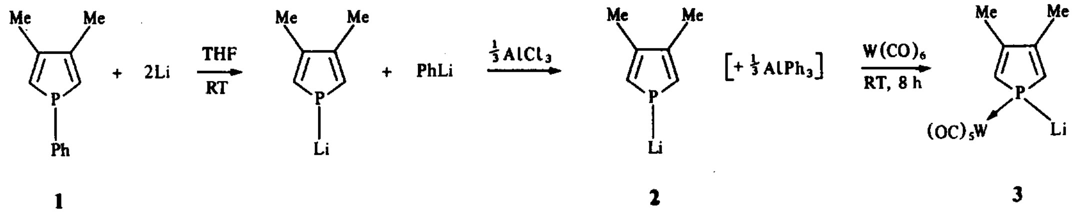
A parallelepipedic crystal of dimensions 0.15 × 0.22 × 0.26 mm was glued at the end of a glass fibre and mounted on a rotation free goniometer head. All quantitative data were obtained using the same diffractometer, graphite-monochromated radiation and standard software in a cold nitrogen gas stream (–100°C). The vertical and horizontal apertures in front of the scintillation counter were adjusted so as to minimize the background counts without loss of net peak intensity at the 2σ level. The total scan width in the θ–2θ flying step-scan used was $\Delta\theta = 1.0 + 0.343\ \mathrm{tg}(\theta)^\circ$, with a step width of 0.05° and a scan speed of 0.02° s^{-1}. 7631 hkl, $\bar{h}kl$, $hk\bar{l}$ and $\bar{h}k\bar{l}$ reflections were recorded (3° < θ < 30°). Three standard reflections measured every hour during the entire data-collection period showed no significant trend. The resulting data-set was transferred to a PDP 11/60 computer, and for all subsequent computations, the Enraf–Nonius SDP/V18 package was used,[16] with the exception of a local data-reduction program.

The raw step-scan data were converted to intensities using the Lehmann–Larson method[17] and then corrected for Lorentz, polarization and absorption factors, the latter computed by the empirical method of Walker and Stuart[18] (transmission factors between 1.00 and 0.81). Averaging of equivalent reflections ($R_i = 0.019$) led to a unique data set of 2942 reflections having $I > 3\sigma(I)$ used for determining and refining the structure.

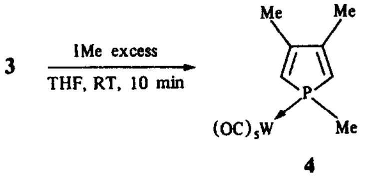
The structure was solved using the heavy-atom method. After refinement of the heavy atoms, a difference-Fourier map revealed maxima of residual electronic density close to the positions expected for hydrogen atoms; they were introduced in structure factor calculations with computed coordinates (C—H = 0.95 Å) and isotropic temperature factors [B_{eqv}(C)] of +1 Å^2 but not refined. Full least-squares refinement converged to $R(F) = 0.029$ and $R_w(F) = 0.060$ $\{\alpha(F^2) = [\sigma^2(\mathrm{count}) + p(I)^2]^{1/2}\}$. The unit-weight observation was 1.32 for $p = 0.08$. A final difference map revealed no significant maxima. The scattering factors coefficients and anomalous dispersion coefficients come, respectively, from Refs 19 and 20.

RESULTS AND DISCUSSION

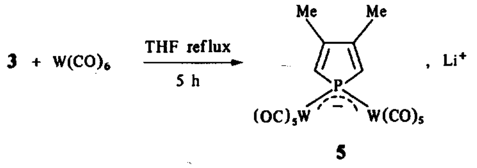
Throughout this study, our starting product has been the readily available 1-phenyl-3,4-dimethylphosphole (**1**).[21] The cleavage of the P–phenyl bond of **1** is achieved by reaction with lithium in THF as usual. Then, phenyllithium is selectively destroyed by adding a stoichiometric amount of anhydrous aluminium trichloride (see Ref. 14). The solution of 3,4-dimethylphospholyllithium (**2**) thus obtained is then allowed to react at room temperature with one equivalent of hexacarbonyltungsten:



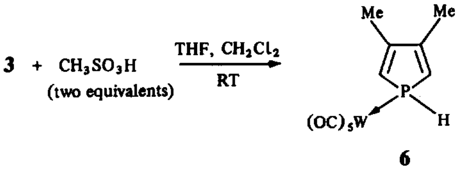
The ^{31}P NMR resonance of **2** at ca +55 ppm (vs external 85% H_3PO_4) slowly disappears and is replaced by a new resonance at −54.8 ppm corresponding to the complexed anion (**3**). The structure of **3** is established by methylation with methyl iodide which gives the already known 1,3,4-trimethylphosphole complex (**4**) [$\delta(^{31}P)$(**4**) −8.4 ppm in THF, $^1J(^{31}P-^{183}W)$ 207.5 Hz].



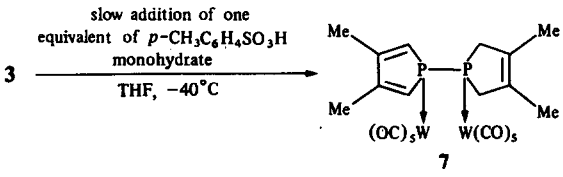
At room temperature, the reaction of **2** with $W(CO)_6$ stops at the level of the monocomplexed anion (**3**) but in refluxing THF, **3** is in turn able to react with another equivalent of $W(CO)_6$ to afford the already described[15] and almost unreactive dicomplexed anion (**5**) which has been previously obtained by allowing **2** to react directly with two equivalents of $W(CO)_5$THF [$\delta(^{31}P)$(**5**) −99.5 ppm in THF].



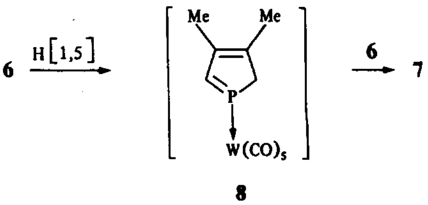
The protonation of **3** is very interesting. When pouring a THF solution of **3** into a CH_2Cl_2 solution of a strong acid such as methanesulfonic acid at room temperature, the sole product is the P–H phosphole complex (**6**) [$\delta(^{31}P)$(**6**) −46 ppm, $^1J(^{31}P-^{183}W)$ 232 Hz, ^1J(P–H) ≃ 322 Hz].



Complex **6** has only a limited stability in THF at room temperature and decomposes completely in ca 4 h to give two dimers (**6a** and **6b**) [$\delta(^{31}P)$ (**6a**) +25.6 ppm, $^1J(^{31}P-^{183}W)$ 237 Hz; and +15.6 ppm, $^1J(^{31}P-^{183}W)$ 229.5 Hz, J(P–P) 14.6 Hz, ^1J(P–H) 285.5 Hz. $\delta(^{31}P)$ (**6b**) −1.8 ppm, $^1J(^{31}P-^{183}W)$ 239.5 Hz; and −29.8 ppm, $^1J(^{31}P-^{183}W)$ 229.5 Hz, J(P–P) 7.3 Hz, ^1J(P–H) 325 Hz]. Both dimers contain one P—H bond and no P—P bond. We suspect that they are formed through addition of the P—H bond of one molecule of **6** to the dienic system of another molecule of **6**. Such dimerizations have been encountered during a study of the protonation of **1** (Quin *et al.*, to be published). Complex **6** can be also prepared by acidic cleavage of the P–SnPh$_3$ complex (**9**) by HCl in methanol (*vide infra*). If the protonation of **6** is either carried out with a weak acid (acetic acid, silica gel) or at low temperature, then the course of the reaction changes and the main product becomes the phospholenophosphole complex (**7**) [$\delta(^{31}P)$ (**7**) +6.0 ppm in THF, $^1J(^{31}P-^{183}W)$ 202 Hz (phosphole cycle); −8.65 ppm, $^1J(^{31}P-^{183}W)$ 220 Hz, ^1J(P–P) 178 Hz (phospholene cycle)] which is sufficiently stable to be isolated in the pure state and completely characterized contrary to **6**, **6a** and **6b**.

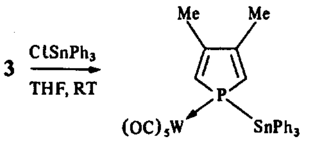


The formation of **7** deserves some comments. We have shown previously[17] that P–H phospholes tend to rearrange through hydrogen [1, 5] sigmatropic shifts to give the very reactive 2H-phospholes. This tendency still exists when P–H phospholes are complexed at phosphorus. Thus the mechanism through which **7** is formed simply involves the addition of the P—H bond of **6** onto the P=C double bond of the corresponding 2H-phosphole complex (**8**).



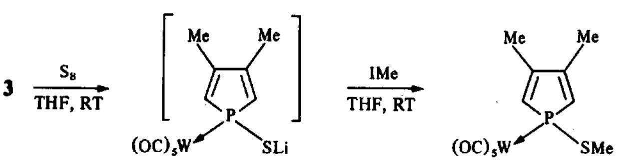
Such a dimerization has already been described in the case of the uncomplexed 2,3,4,5-tetraphenylphosphole.[22]

As mentioned earlier, it is possible to prepare the P–SnPh$_3$ complex (**9**) [$\delta(^{31}P)$ (**9**) −66 ppm in THF, $^1J(^{31}P-^{183}W)$ 190 Hz, $^1J(^{31}P-^{119}Sn)$ 88 Hz] by reaction of the appropriate tin chloro derivative with **3**.



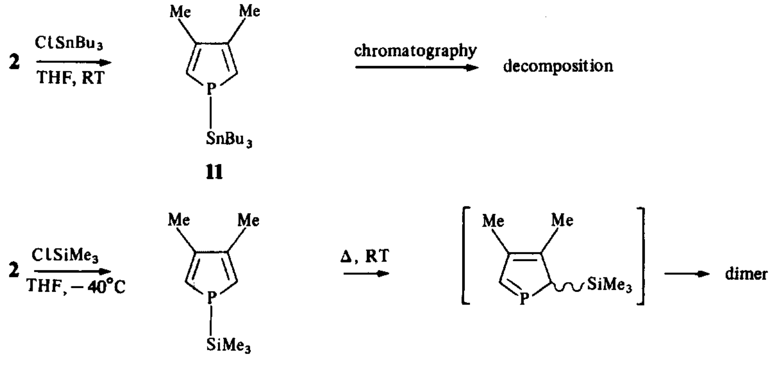
9

Complex **9** can be purified by chromatography and is obtained in ca 68% yield. Complex **3** is also able to react cleanly with sulphur at room temperature. The P–SLi complex thus obtained can be alkylated at sulphur by methyl iodide to give the P–SMe complex (**10**) in 70% yield [$\delta(^{31}P)$ (**10**) 19.6 ppm in THF, $^1J(^{31}P-^{183}W)$ 222 Hz].



10

It is interesting to compare what occurs during the syntheses of **9** and **10** with what is observed when attempting similar reactions with the uncomplexed anion **2**. The reaction of **2** with *n*-Bu$_3$SnCl in THF gives the expected P–SnBu$_3$ phosphole (**11**) [$\delta(^{31}P)$ (**11**) −62.7 ppm in THF] but an attempted purification by chromatography led to decomposition. This decomposition probably occurs through hydrolysis and (or) oxidation of the P—Sn bond of **11** but can also involve a [1,5] migration of the SnBu$_3$ group similar to what happens when **6** is converted into **7** by chromatography on silica gel. Indeed, such a migration has been observed in a related case when attempting to prepare silylphosphole (**12**).

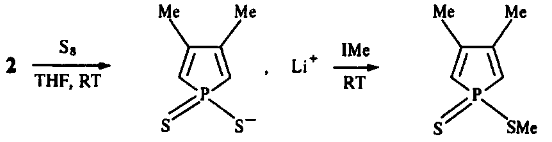


11

12

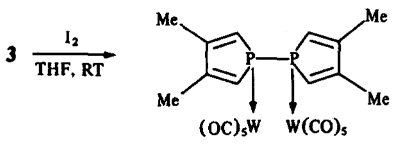
This silylphosphole [$\delta(^{31}P)$ (**12**) −50 ppm in THF] immediately rearranges to give a P—P bonded dimer [$\delta(^{31}P)$ +0.8 and −21.0 ppm in THF, ^1J(P–P) 195 Hz]. Even though we are unable to assign a precise formula to this dimer because it is very sensitive toward oxidation and hydrolysis and cannot be purified, the formation of a P—P bond necessarily involves a migration of the silyl group. Thus, the reasonable stabilities of both complexes **6** and **9** clearly demonstrate that P–W(CO)$_5$ complexation not only stabilizes phospholes toward oxidation and hydrolysis but also toward [1,5] sigmatropic shifts. It may be noted here that we[23] and Jutzi[24] have already demonstrated that P-complexation by W(CO)$_5$ or Cr(CO)$_5$ quenches the fluxionality of some selected cyclopentadienylphosphines which occurs through H and PR$_2$ [1,5] shifts. The freezing of these various types of migrations probably involves a common mechanism.

P-complexation also alters the course of the reaction of phospholyl anion with sulphur. Indeed, monosulphurization of **2** proved to be impossible. The reaction goes directly to the dithiophosphinic anion which can be easily alkylated by methyl iodide to give **13** [$\delta(^{31}P)$ (**13**) +62.9 ppm in THF].



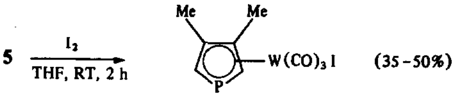
13a **13**

Finally, we have also studied the reaction of **3** with iodine. Here, the behaviour of **3** appears to be exactly similar to that of **2** (see Ref. 14): in both cases, a P—P bond is created. Complex **14** [$\delta(^{31}P)$ (**14**) +5.9 ppm in THF] is thus obtained in 55% yield.



14

The study of the reactivity of the dicomplexed anion (**5**) has been much less complete. In fact **5** is far less reactive than **3**. The protonation of **5** is difficult and requires a strong acid. It gives an interesting stable 2H̲-phosphole complex which has been described previously.[15] Quite unexpectedly, the reaction of **5** with iodine also affords a very interesting result: the first known η^5-phospholyl-tungsten complex (**15**) [$\delta(^{31}P)$ (**15**) −31.5 ppm in THF] is thus obtained.



15

The crystal structure of **15** was established by X-ray diffraction and consists of discrete molecules only linked by van der Waals' contacts; there are no non-usual intermolecular contacts.* Figure 1 displays one molecule of **15**. Table 1 gives selected bond lengths and angles with their estimated standard deviations. The tungsten atoms are nine-coordinated: three carbonyl and the iodine atom lie on one side whereas the η^5-phospholyl ring occupies the opposite side of the coordination polyhedron. C7, C8, C9 and I form a roof: I is outside the plane containing C7, C8 and C9 by 0.421(1) Å on the same side as W; the dihedral angle between the planes C7–C8–C9 and I–C8–C9 is 9.5°. The W—I bond length of 2.8331(5) Å is not significantly different from that reported for $WI_2(OCMe_3)_6$, 2.8293(8).[25] The three W—C (carbonyl) bond lengths range from 1.982(8) to 2.017(6) Å and the W—C≡O bond angles have values near to 180°. The W atom is not equidistant from the four C atoms of the phospholyl core: the W—C1 bond length is shorter than the three other bond lengths, thus the projection of W on the C1 → C4 plane is out of the line joining the P atom to the middle of the C2—C3 bond in the direction of C1.

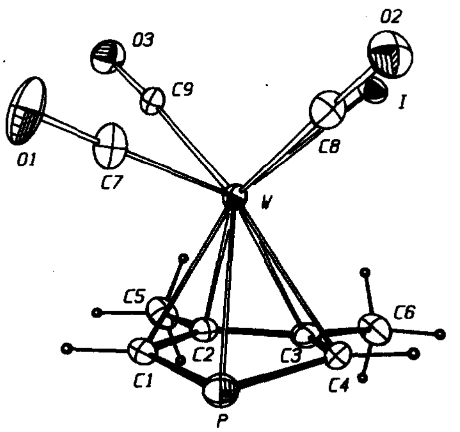


Fig. 1. Structure of complex **15**. The heavy-atom ellipsoids are scaled to enclose 50% of the electron density, hydrogen atoms have arbitrary radii.

The carbon atoms C1–C4 are coplanar within experimental error; the phosphorus atom is outside from this mean plane by 0.150(3) Å and the tungsten atom by 1.963(0) Å. As expected, the W—P bond length of 2.516(2) Å is greater than those found in pure W—P σ-bonds[2,15] but less than those in complexes having some π character in their W—P bond.[15] The dihedral angle between the mean planes of these four carbon atoms and P–C1–C4 is equal to 6.8°, a value greater than those found in η^5-phosphacymantrenes[8] or diphosphaferro-

Table 1. Selected bond lengths (Å) and angles (°) with their estimated standard deviations

W—I	2.8331(5)	I—W—C7	131.6(3)
W—P	2.516(2)	I—W—C8	76.5(2)
W—C1	2.302(7)	I—W—C9	74.8(2)
W—C2	2.380(7)	C7—W—C8	78.3(3)
W—C3	2.443(7)	C7—W—C9	76.9(3)
W—C4	2.342(7)	C8—W—C9	110.1(3)
W—C7	1.982(8)	C1—P—C4	88.3(4)
W—C8	2.004(8)	P—C1—C2	113.7(6)
W—C9	2.017(6)	P—C4—C3	112.9(6)
P—C1	1.775(8)	C1—C2—C3	112.0(7)
P—C4	1.771(6)	C2—C3—C4	112.3(7)
C1—C2	1.41(1)	C1—C2—C5	122.8(7)
C3—C4	1.43(1)	C4—C3—C6	123.0(8)
C2—C3	1.40(1)	C3—C2—C5	125.0(7)
C2—C5	1.51(1)	C2—C3—C6	124.6(8)
C3—C6	1.51(1)	W—C7—O1	178.1(7)
C7—O1	1.14(1)	W—C8—O2	178.7(7)
C8—O2	1.13(1)	W—C9—O3	176.5(7)
C9—O3	1.121(8)		

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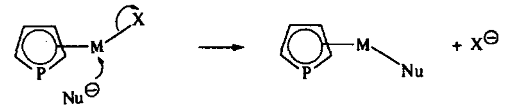
* Tables of atomic positional parameters and thermal parameters and lists of F_o/F_c values have been deposited as supplementary data with the Editor, from whom copies are available on request. Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.

cenes,[11] suggesting some loss of aromaticity of the phospholyl ring in complex **15**. The bond lengths and angles in the phospholyl ring are not significantly different from those found in η^5-phosphacymantrenes.[8]

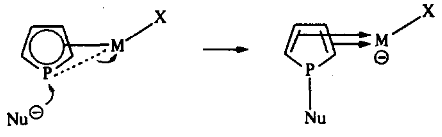
From a spectroscopic point of view, we have noted one very peculiar characteristic of this π-complex. No NMR coupling is visible between ^{31}P and ^{183}W nuclei, whereas the P—W bond length lies close to the normal value. This property seems to be characteristic of tungsten π-complexes involving P═C delocalized multiple bonds. Indeed, a similar situation has been encountered in the case of $\eta^2[CH_2{=}PCl]W(CO)_5$.[26]

Theoretical studies[27–29] have shown that the main difference between corresponding η^5-cyclopentadienyl and η^5-phospholyl complexes lies in the presence of a low-lying LUMO highly localized at phosphorus in the latter case. Since complex **15** is the first known η^5-phospholyl complex in which the P ring shares the coordination sphere of a metal with an halogen, it offered us the opportunity to compare the reactivities of P–metal and metal–halogen bonds toward nucleophiles. Two types of attacks could be envisaged: (a) the "normal" attack at the metal with loss of an halide ion; (b) the "abnormal" attack at phosphorus with cleavage of the phosphorus–metal bond.

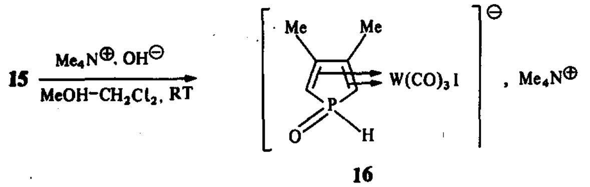
(a)



(b)

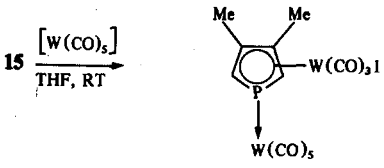


Apparently the "abnormal" attack is preferred at least in the case of the hydroxide ion.



16

Complex **16** [$\delta(^{31}P)$ (**16**) +38.8 ppm in acetone, $^1J(P\text{–}H)$ 532 Hz] is thus obtained in 75% yield. Finally, it is also interesting to note that, during the synthesis of **15**, a P → $W(CO)_5$ complex of **15** (**17**) is formed as a by-product [$\delta(^{31}P)$ (**17**) −14 ppm in $CDCl_3$, $^1J(^{31}P\text{–}^{183}W)$ 274 Hz].



17

Here of course, a normal ^1J coupling is observed between P and the $W(CO)_5$ tungsten. The formation of **17** from **15** is exactly similar to the various P-complexations observed with phosphamantrenes,[30] phosphaferrocenes[26] and diphosphaferrocenes.[32]

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